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Topologically Driven Compatibility Enhancement in the Mixtures of Rings and Linear Chains

A.R. Khokhlov (1) and S.K. Nechaev (2,*,**)

(1) Physics Department, Moscow State University, 119899 Moscow, Russia
(2) L.D. Landau Institute for Theoretical Physics, 117940 Moscow, Russia

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Abstract. — The thermodynamics of the bicomponent melts of linear chains A and unknotted unentangled closed chains B (trivial rings) is considered within the framework of the usual Flory approach. It is shown that such melts exhibit a compatibility enhancement in comparison with the corresponding melts of linear chains. The reason for such effect is due to the topological entropy gain of mixing of A- and B-chains: if B-chains are unentangled since the A-chains play the role of a “diluent” softening the topological restrictions imposed on the B-chains. This result is in agreement with recent experimental findings of McKnight et al.

1. Introduction

The problem of compatibility in the mixtures of linear macromolecules is now well-established. If two melts of linear chains A and B are mixed, their compatibility is governed by the corresponding Flory parameter, \( \chi \), describing the relative thermodynamic favorability for A-B contacts [1]. Within the framework of the Flory lattice model the free energy of mixing is then expressed (see [1,2]) as

\[
\frac{F}{kTn_0} = \frac{\bar{\Phi}_A}{N_A} \ln \frac{\Phi_A}{N_A} + \frac{\bar{\Phi}_B}{N_B} \ln \frac{\Phi_B}{N_B} + \chi \bar{\Phi}_A \Phi_A
\]  

(1)

where \( \bar{\Phi}_i \) is the volume fraction of the chain \( i \) in the mixture (\( i = [A, B] \)), \( N_i \) is the number of monomer units in the chain \( i \), \( T \) is the temperature, \( k \) Boltzmann constant and \( n_0 \) is the total number of lattice sites. The first two terms in equation (1) represent the translational entropy of the chains A and B, while the second term is the interaction energy. Equation (1) gives the phase diagram (see Fig. 1) with the critical point at

\[
\chi^{(0)}_{\text{cr}} = \frac{(N_A^{1/2} + N_B^{1/2})^2}{2N_AN_B}
\]  

(2)

(*') Current address: Institut de Physique Nucléaire, Division de Physique Théorique, 91406 Orsay Cedex, France
(**) e-mail: nechaev@landau.ac.ru

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For $N_A = N_B = N$ this gives $\chi_{cr}^{(0)} = 2/N \ll 1$; thus even slight positive values of $\chi$ are enough to induce the uncompatibility of the mixture. This effect is known to be due to the small value of the entropy of mixing: according to equation (1) only chains as a whole, not individual monomer units, possess the entropy of independent translational motion.

In the present paper we address the question how the above-mentioned arguments will change if one of the components (say, B) is the closed ring macromolecules. On the one hand, since chains A are still linear macromolecules, the set of their conformations in the thermodynamic limit is insensitive to the fact that chains B are rings. On the other hand, due to the existence of topological interactions [2-4], the conformational set of the chains B depends on their mutual topological state. We will assume that the closed macromolecules B form trivial rings (i.e., they are unknotted), and moreover that chains B are not entangled with each other. Such a system of unknotted unentangled rings can be prepared in dilute solutions of chains B, and then concentrated upon the evaporation of the solvent.

The main effect which we would like to describe in the present paper is the compatibility enhancement in the melts of linear chains A and rings B in comparison with the corresponding melt of linear chains. The physical explanation of the phenomenon is very simple (see Fig. 2). Keeping the chains B in the concentrated system unentangled imposes significant restriction on the possible chain conformations, i.e., leads to a large entropy loss. This entropy loss is larger for higher concentration of B-chains. Since for the mixed A/B-system (Fig. 2b) the concentration of B-chains is lower than that for the demixed B-rich phase (Fig. 2a), the thermodynamic favorability for the mixed situation (i.e., compatibility enhancement) driven by the topological effects becomes apparent.

Below we will present the qualitative theory for the described effect. The topological state of the system of unentangled B-chains is described within the theory of “crumpled globule” state proposed earlier in [5,6]. Therefore, in the next Section we start with the brief reminder of the main ideas of references [5,6]. In the Section 3 we derive the expression for the free energy for the mixture of linear open chains A and rings B analogous to the equation (1) for the melt of linear chains and analyze the corresponding phase diagram. Some discussion of the
results and the final conclusions are contained in Section 4.

The idea to consider the thermodynamics for the mixtures of linear chains and rings was formulated after appearance of the experimental results of McKnight et al. for the blends of biphenol-A-carbonate cyclic oligomers and styrene-acrylonitrile copolymers [7] where the tendency for the compatibility enhancement was demonstrated. A more detailed experimental study of this effect would allow to verify the theoretical predictions of the present paper.

2. Collapsed Phase of Unknotted Ring Polymer

The chain statistics in the concentrated solutions and melts of unentangled unknotted ring polymers was considered by the present authors more than ten years ago [8] (see also Refs. [9, 10]). It was shown that the resulting chain conformations are close to that of practically completely segregated collapsed globules; the segregation is caused by the impossibility of significant chain interpenetration without mutual entanglement. Thus, to describe the entropy of B-chains in Figure 2 it is necessary, first of all, to be able to write down the free energy of isolated collapsed unknotted ring polymer B. This problem was solved in [5,6] on the basis of the so-called “crumpled globule” concept.

Take closed nonselfintersecting polymer chain of length \( N \) in the trivial topological state \(^\text{(1)}\).

\(^{\text{(1)}}\) The fact that the closed chain cannot intersect itself causes two types of interactions: a) volume interactions which vanish for infinitely thin chains and b) topological constraints which remain even for chain of zero thickness.
In the poor solvent (at \( T < \theta \), where \( \theta \) is the \( \theta \)-temperature) the formation of the collapsed globular structure becomes thermodynamically favorable [12]. Supposing that the globular state can be described in the virial expansion we introduce as usual two- and three-body interaction constants: \( B = b\tau < 0 \) (\( \tau = \frac{T-\theta}{\theta} \)) and \( C = \text{const} > 0 \). But in addition to the standard volume interactions we should take into account the non-local topological constraints which obviously have a repulsive character.

The condition for a closed polymer to form a trivial knot changes significantly all thermodynamic properties of a macromolecule and leads to specific non-trivial fractal properties of a line representing the chain trajectory in a globule. Such structure is called crumpled globule (see for details Refs. [5,6]).

It is well-known that in a poor solvent there exists some critical chain length, \( g_{\text{cr}} \), such that chain pacts which have length bigger than \( g_{\text{cr}} \) collapse [5]

\[
\frac{g_{\text{cr}}}{R_{g_{\text{a}}}^3} \simeq \rho
\]

Here \( \rho \) is the concentration of monomer units within the globule and \( R_{g_{\text{a}}} \simeq g_{\text{cr}}^{1/2} a \). Thus, we have

\[
g_{\text{cr}} \simeq \frac{1}{(\rho a^3)^2} = \left( \frac{C}{b\tau a^3} \right)^2
\]

(3)

Therefore, \( g_{\text{cr}} \) depends on the temperature deviation \( \tau \) from the \( \theta \)-point, the Kuhn segment length \( a \) and the parameters \( b \) and \( C \), connected with the volume interactions. Taking long enough chain these \( g_{\text{cr}} \)-link parts were defined in [5] as new block monomer units (crumples of minimal scale).

Consider now the part of a closed (ring-like) chain with several block monomer units. This new part should again collapse in itself, i.e. should form the crumple of the next scale if other chain parts do not interfere with it. The chain of such new subblocks (crumples of new scale) collapses again and so on till the chain as a whole (see Fig. 3) forms the largest final crumple. Thus the procedure is completed when all the links are united into one crumple of the largest scale. This state of the collapsed globule is modified for linear chains due to the reptation-like motion of the chain ends which ensures the further chain self-knotting. However for rings reptations are forbidden and this crumpled state is final, i.e. corresponds to the thermodynamic equilibrium.

It may seem that due to space fluctuations of the chain parts all that crumples could penetrate each others with the loops, destroying the self-similar scale-invariant structure described above. However in reference [5] it was shown that if the chain length in a crumple of an arbitrary scale exceeds \( N_{0} \) times the value of \( g_{\text{cr}} \) then the crumplings coming in contact do not mix with each others and remain segregated in space. Here it should be recalled that \( N_{0} \) is the characteristic distance between neighboring entanglements along the chain expressed in number of segments and, as a rule, the values of \( N_{0} \) lie in the range 30-300. Actually, \( g_{\text{cr}} = (\rho a^3)^{-2} \) is the mean length of the chain part between two neighboring (along the chain) contacts with other parts; consequently \( N_{0} g_{\text{cr}} \) is the mean length of the chain part between topological contacts (entanglements). Of course, for the phantom chains, Gaussian blobs of size \( g_{\text{cr}} \) are strongly overlapped with others because pair contacts between monomers are screened in \( \theta \)-conditions (see Ref. [12]). However for nonphantom chains these pair contacts are topologically essential because chain crossings are prohibited for any value and sign of the virial coefficient.

Thus, the entropy loss connected with the crumpled state formation per whole globule of volume \( V \) can be estimated as follows:

\[
S \simeq -\frac{N}{g_{*}^2} k
\]

(4)
where

\[ g^* = N_c g_{c1} = N_e (\rho a^3)^{-2} = N_e \left( \frac{C}{b r a^3} \right)^2 \]  \hspace{1cm} (5)

The experimental verification of the self-similar fractal structure of the collapsed unknotted ring polymer proposed in references [5,6] was performed recently. One of the ways to support the "crumpled globule" (CG) concept comes from its indirect manifestations in dynamic and static properties of different polymer systems. Among predictions and their justifications made on the basis of CG-concept we could mention: a) two-stage dynamics of collapse of the macromolecule after abrupt changing of the solvent quality, found in recent light scattering experiments by Chu and Ying (Stony Brook) [13] b) recent paper [14] where the authors claim
the direct observation of the crumpled globule; c) successive quantitative explanation of the collapse of N-isopropylacrylamide gel collapse in pure water \[6\].

In the next Section we will use the expression (4) to obtain the free energy of the concentrated system of unknotted unentangled ring-like macromolecules taking into account the result of reference \[5\] where it was shown that for this case the conformation of each ring chain is similar to that of the unknotted crumpled globule.

3. Thermodynamics of Mixture of Linear and Ring Chains

Let us assume that we have a bicomponent melt of linear polymers A and ring-like macromolecules B. The notations will be the same as in the Introduction.

In the framework of the conventional mean-field theory the total free energy, \(F\), of the system per volume unit we can write as follows:

\[
F = F_0 + F_{\text{top}} \tag{6}
\]

where \(F_0\) is the standard free energy of the mixture of two polymers (see Eq. (1)), whereas \(F_{\text{top}}\) denotes the contribution to the free energy coming from the fact that B-chains are unknotted and unentangled.

According to equations (4) and (5) the term \(F_{\text{top}}\) can be estimated as follows

\[
F_{\text{top}} = -TS \simeq kT \frac{N_B}{N_e} (\rho a^3)^2 \tag{7}
\]

where the relation between the polymer volume fraction, \(\Phi_B\), the concentration, \(\rho\), and the chain segment length, \(a\), in the lattice theory is \(\Phi_B = \rho a^3\). Thus, equation (7) reads

\[
F_{\text{top}} \simeq kT n_0 \frac{1}{N_e} \Phi^3 \tag{8}
\]

In deriving of equation (8) we just have taken into account the effect described in the Introduction: the higher is the concentration of the unentangled rings B the larger is the penalty connected with the formation of smaller crumples.

Substituting equations (1) and (8) in the expression (6) and taking into account the incompressibility condition \((\Phi_A + \Phi_B = 1)\), we get

\[
\frac{F}{kT n_0} = \frac{\Phi}{N_A} \ln \Phi + \frac{1 - \Phi}{N_B} \ln (1 - \Phi) + \chi \Phi (1 - \Phi) + \frac{1}{N_e} \Phi^3 \tag{9}
\]

where we denoted \(\Phi \equiv \Phi_B = 1 - \Phi_A\).

Therefore, we obtained an extra item in the free energy (last term in Eq. (4)) which is due to the topological interactions. This term favors smaller values of \(\Phi_B\), i.e., the lower loss in the entropy due to the crumpled formation. Of course, it should be mentioned that the new "topological" term is only estimated, not exactly calculated, therefore one should put some numerical coefficient of order of unity before this term. However, since the value of \(N_e\) is always only loosely defined, we omit this coefficient for the sake of simplicity of the subsequent analysis where we pay attention mainly to the qualitative effects.
The phase diagram which follows from the expression (9) for the free energy is drawn in Figure 4. The compatibility enhancement effect because of the topological interactions between the unentangled chains B is apparent. The effect is larger for smaller concentrations of chains B and larger values of $N_A$ (cf. Figs. 4a and 4b). For $N_A \sim N_B \sim N \gg N_e$ the shift of the
critical point is very significant. In this limit we have
\[ \chi_{cr}^{(0)} \sim \frac{1}{N} \quad \text{for the mixture of two linear chains} \]
\[ \chi_{cr} \sim \frac{1}{(N_e N)^{1/2}} \quad \text{for the mixture of linear and ring chains} \] (10)

4. Discussion and Conclusion

In this paper we have shown that there is a compatibility enhancement effect in the mixture of linear chains and unknotted unentangled rings. For long enough linear chains this effect can be very significant. The experimental works confirming the existence of the phenomenon were done earlier [7].

Of course, the calculation of the specific value of this effect performed above is very approximate. It uses the picture of the concentrated system of unentangled rings as the collection of segregated crumpled globules. Probably, these assumptions are too strong, especially, as regards mutual segregation of chains due to topological repulsion. We could refer to the work of Cates and Deutsch [9] dealing with the statistics of the melt of unentangled rings.

The authors of [9] got (2):
\[ R_G \sim N^{2/5} \] (11)
and
\[ \tilde{F}_{\text{top}} \sim N^{1/5} \] (12)
for the gyration radius and the free energy of the ring chain in the melt of unentangled closed polymers.

In order to compare our expression for \( F_{\text{top}} \) (Eq. (8)) with the topological contribution derived on the basis of equation (12), we should replace the equation (4) with the following one
\[ \tilde{S} \simeq -\left( \frac{N}{g_*} \right)^{1/5} k \] (13)
what leads to the new form of the topological contribution in equation (6)
\[ \tilde{F}_{\text{top}} \simeq kTn_0 \frac{1}{N_e^{1/5} N^{4/5}} \Phi^{7/5} \] (14)
(compare to Eq. (8)). The equation (9) should be replaced now by the following one:
\[ \frac{F}{kTn_0} = \frac{\Phi}{N_A} \ln \Phi + \frac{1 - \Phi}{N_B} \ln(1 - \Phi) + \chi \Phi(1 - \Phi) + \frac{1}{N_e^{1/5} N^{4/5}} \Phi^{7/5} \] (15)

Despite this expression differs from equation (9), it predicts the effect of compatibility enhancement as well and does not change it physical explanation. However in the case of equation (15) for \( N_A \sim N_B \sim N \) the shift of the critical point \( \chi_{cr} \) is less significant:
\[ \tilde{\chi}_{cr} \sim \frac{1}{N_e^{1/5} N^{4/5}} \] (16)

Our point of view is such that the way of derivation of equations (11) and (12) in the paper [9] is not scale-invariant, nevertheless some of theoretical predictions of Cates and Deutsch are
in very good agreement with experimental data. So, we believe that further experiments on compatibility enhancement on the mixture of rings and linear chains will show which expression for the topological contribution equation (8) or equation (14) works better.

The additional physical interest to the thermodynamical properties of the melt of linear chains A and rings B comes from the fact that due to the existence of topological interactions the entropy of the system becomes highly nonlocal without the direct chemical connection between the components A and B. From the experience with other polymer systems [15–17] we know that such nonlocality coupled with the energetic interactions of the components leads to the microphase separation transition analogous to that in block-copolymers [18]. Therefore, for the present system we may hope to have another new effect — the topologically involved microphase separation. The study of this latter effect will hopefully bring new important information on the entanglement properties of polymer chains.

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